

FORMIC ACID: MANUFACTURING OF FORMIC ACID



SUBMITTED TO: MAAM SADIA RANI SUBMITTED BY: NIMRAH YOUNAS ROLL NO.: BSF 2106698

SESSION :2021-2025 SEMESTER: 4TH MORNING

COURCE NAME: INDUSTRIAL CHEMISTRY (CHEM2113)

DEPARTMENT OF CHEMISTRY UNIVERSITY OF EDUCATION D.G. KHAN CAMPUS

TABLE OF CONTENTS

1. INTRODUCTION

2

2. DISCOVERY

2

2.2 NATURAL EXTRACTION

2

2.3 ARTIFICIAL SYNTHESIS

2

3. DIMER FORM OF FORMIC ACID
3

4. MANUFACTURING OF FORMICACID

3

4.1 FROM SODIUM FORMATE

3

4.2 FROM PRODUCER GAS

4

4.3 FROM METHYL FORMATE

4

4.4 FROM BY-PRODUCTS

5

5.ENGINEERING ASPECTS

5

6. USES OF FORMIC ACID

6

7. REFERENCE

ճ

FORMIC ACID: MANUFACTURING OF FORMIC ACID

1. INTRODUCTION

Formic acid, HCOOH is the simplest carboxylic acid and also called as methanoic acid. It is a colorless liquid having a highly pungent, penetrating odor at room temperature. It is miscible with water and most polar organic solvents, and is somewhat soluble in hydrocarbons.

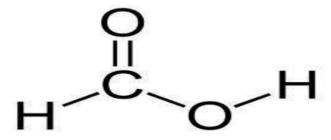


Fig1; chemical structure of formic acid.

2. DISCOVERY

2.1 NATURAL EXTRACTION

In the 15th century it was aware that venom of bee, ant stings and ant hills give off an acidic vapor. John Ray described the isolation of formic acid by distillation of large numbers of ants in 1671. Ants secrete the formic acid for attack and defense purposes. The name formic acid comes from the Latin word for ant ,formica, referring to its early isolation by the distillation of ant bodies.

2.2 ARTIFICIAL SYNTHESIS

Joseph Gay Lussac first synthesized formic acid from hydrocyanic acid by the French chemist. Marcellin Berthelot, developed a synthesis from carbon monoxide in 1855, the method with some modifications still in used.

3. DIMER FORM OF FORMIC ACID

Formic acid consists of hydrogen bonded dimers rather than individual molecules in hydrocarbons and in the vapor phase. Due to its tendency to hydrogen bond, gaseous formic acid does not obey the ideal gas law. Solid formic acid consists of an effectively endless network of hydrogen bonded formic acid molecules. It also forms a low boiling azeotrope with water and liquid formic acid also trends to supercool. Esters, salts and the anion derived from formic acid are referred to as formates.

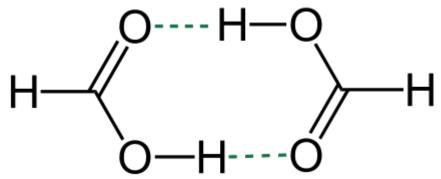


Fig 2; dimer form of formic acid

4. MANUFACTURING OF FORMIC ACID

4.1 FROM SODIUM FORMATE

Raw material

4 | Page

Formic acid Sodium hydroxide Carbon monoxide Sulfuric acid

Reaction

$$2HCOONa + H_2SO_4 ----> 2HCOOH + Na_2SO_4 \\ 90-95\% \ yield$$

• Manufacturing process

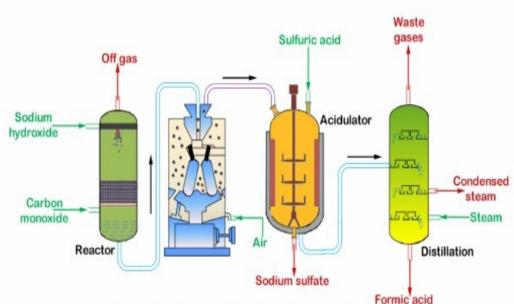


Figure: Manufacture of Formic acid from sodium formate

Fig3;Block diagram of manufacturing of formic acid from sodium formate

Sodium hydroxide was charged into a reactor equipped with agitator a packed tower. Carbon monoxide, freed from carbon dioxide which is obtained by the incomplete combustion of coke is reacted with the caustic soda at 150 $\,$ 200 $\,$ 0C temperature under a pressure of 100150 psi. The resulting reaction product is crude sodium formate.

Crude sodium formate was acidified with dilute sulfuric acid, resulting formic acid distilled off. Due to the proximity of the formic acid and water boiling points, only dilute formic acid an be obtained by separating it from Na_2SO_4 by distillation. The yield based on sodium hydroxide charged is 90 95%.

4.2 FROM PRODUCER GAS

As an alternate procedure, producer gas (carbon monoxide and hydrogen) and a dilute sodium hydroxide solution (25 – 30% NaOH) may be reacted under essentially the same condition. The effluent liquor may be dried to yield sodium formate.

4.3 FROM METHYL FORMATE

$$CH_3OH + CO \rightarrow CH_3OOCH$$

 $CH_3OOCH + H_2O \rightarrow HCOOH + CH_3OH$

The acid hydrolysis of methyl formate also results into formic acid. Methanol and carbon monoxide are reacted at about 200°C under the pressure of 20 -25atm to give methyl formate. By the action of water and catalytic amounts of sulfuric acid, methyl formate is converted to dilute formic acid and methanol. Essentially anhydrous or concentrated formic acid may be obtained by subjecting methyl formate to reaction with glutaric or oxalic acid with an admixed esterification catalyst such as sulfuric acid, Formic acid is liberated while methyl esters of the dibasic acid are hydrolyzed with water to liberate methanol. The regenerated dibasic acid is recovered.

4.4 FROM BY-PRODUCTS

In the manufacturing of acetic acid by the catalytic oxidation of paraffin hydrocarbons formic acid is obtained as a by-products. Some company also recovers formic acid from wood pulp cooking waste.

5. ENGINEERING ASPECTS

❖ Effects of acid concentration

The addition of concentrated sulfuric acid to dry sodium formate results in quite extensive decomposition with formation of carbon monoxide. The decomposition is minimized by adding concentrated sulfuric acid to slurry of powdered sodium formate.

* Amount of catalyst

Formic acid from carbonylation of methanol in liquid phase is carried out with aid of basic catalyst such as sodium methoxide .The amount of water and CO_2 in starting material must be minimized because they cause deactivation of catalyst.

Thermodynamics and kinetics

Typical reaction conditions appear to be 80° C, 44 atm pressure and 2.5% w/w of catalyst. The hydrolysis of methyl formate is technologically demanding for a number of reasons. The equilibrium of hydrolysis is relatively unfavorable. It depends on the concentration of water and favors the use of high stoichiometric excesses of water, Due to presence of highly volatile methyl formate. Formic acid is a sufficiently strong acid to catalyze the re-esterification reaction.

6. USES

- ❖ Formic acid is used as preservative and antibacterial agent in livestock feed. It also added to feed to kill E. coli bacteria in the poultry industry.
- ❖ In the production of leather including tanning, dyeing and finishing of textile because of its acidic nature.
- ❖ As a coagulant in the production of rubber.
- ❖ In place of mineral acids for various cleaning products such as lime scale remover and toilet bowl cleaner.
- ❖ For formulation of methyl aniline to N-methylformanalide in toluene
- ❖ As a volatile pH modifier in HPLC and capillary electrophoresis.
- Treatment of formic acid with sulfuric acid is a convenient source of carbon monoxide, as it decomposed by sulfuric acid.

7. REFERENCE

Patel. N.K; Head & Associate Professor of Botany, sheth M.N Science college, Patan. Lecture; 7 module; 2.